19CH201 - ENGINEERING

CHEMISTRYUNIT-1

ELECTROCHEMISTRY

Ion-Selective Electrodes (ISE)

Ion-selective electrodes are the electrodes having the ability to respond only to a particular ions, and develop potential, ignoring the other ions in a mixture totally. The potential developed by an ion-selective electrode dependsonly on the concentration of particular ions.

Example: Glass Electrode

The glass membrane of the glass electrode is only selective to H^+ ions onlyin a mixture.

Glass Electrode (Internal Reference Electrode)

Construction

A glass electrode consists of thin-walled glass bulb (the glass is a specialtype having low melting point and high electrical conductivity) containing a Pt wire in 0.1M HCl (Fig.1.5). The glass electrode is represented as

Pt, 0.1 M HCl / Glass

HCl in the bulb furnishes a constant H^+ ion concentration.

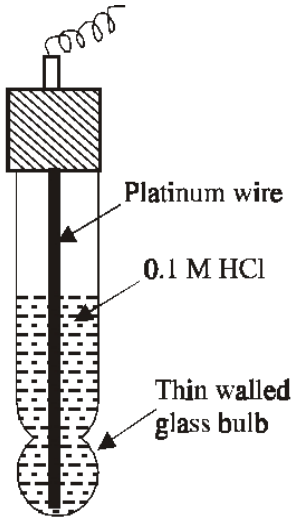

Fig. 1.5 Glass electrode

Glass electrode is used as the "internal reference electrode". The pH of the solutions, especially coloured solutions containing oxidizing or reducing agents can be determined. The thin walled glass bulb called glass membrane functionsas an ion-exchange resin, and an equilibrium is set up between the Na^+ ions of glass and H^+ ions in solution. The potential difference varies with the H^+ ion concentration, and its emf is given by the expression

$$E_G = E°_G + 0.0592\ pH$$

Measurement of pH by glass electrode

Determination of pH of a Solution using Glass Electrode

The glass electrode is placed in the solution under test and is coupledwith saturated calomel electrode as shown in the figure 1.6.

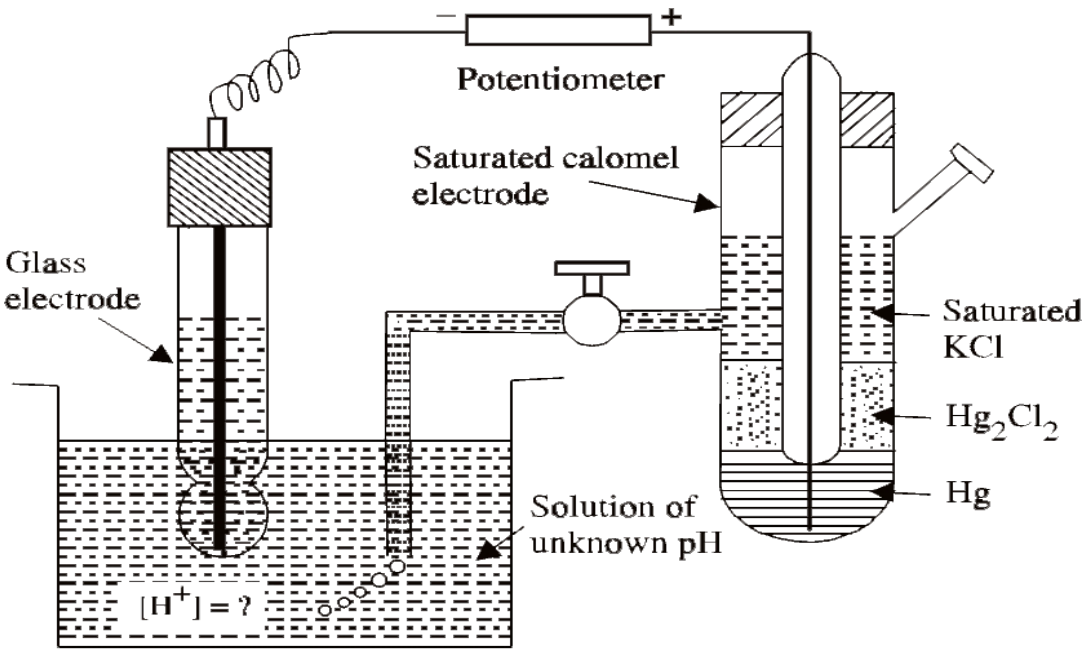

Fig. 1.6 Determination of pH by using glass electrode

The emf of the cell is measured. From the emf, the pH of the solution is calculated as follows

$$E_{cell} = E_{right} - E_{left}$$

$$E_{cell} = E_{cal} - E_G$$

$$= E_{cal} - (E°_G + 0.0592\ pH)$$

$$= E_{cal} - E°_G - 0.0592\ pH$$

$$pH = \frac{E_{cal} - E°_G - E_{cell}}{0.0592} \qquad \therefore E_{cal} = 0.2422\ V$$

$$\therefore pH = \frac{0.2422 - E°_G - E_{cell}}{0.0592}$$

Advantages of Glass Electrode

i. It can be easily constructed and readily used.
ii. The results are accurate.
iii. It is not easily poisoned.
iv. Equilibrium is rapidly achieved.

Disadvantages (Limitations)

i) Since the resistance is quite high, special electronic potentiometers areemployed for measurement.

(ii) The glass electrode can be used in solutions only with pH range of 0 to 10. However above the pH 12 (high alkalinity), cations of the solutionaffect the glass and make the electrode useless.

Applications of ISEs

(i) ISEs are used in determining the concentrations of cations like H^+, Na^+, K^+, Ag^+, Li^+.

(ii) ISEs are used for the determination of hardness Ca^{2+} and Mg^{2+} ions).

(iii) Concentrations of anions like NO_3^-, CN^-, S^{2-}, halides (X^-) can be determined.

(iv) ISEs are used in the determination of concentration of a gas by using gas-sensing electrodes.

(v) pH of the solution can be measured by using gas-sensing electrode.